

## Gelatin films plasticized with a simulated biodiesel coproduct stream

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**Abstract.** In order to explore the possibility of substituting an unrefined biodiesel coproduct stream (BCS) for refined glycerol as a polymer plasticizer we have prepared cast gelatin films plasticized with a simulated BCS, i.e., mixtures of glycerol and some of the typical components found in BCS (methyl linoleate, methyl oleate, linoleic acid, and oleic acid). We measured the tensile properties as a function of plasticizer composition, and analyzed the specific effect of each individual component on tensile properties. We found that it is the unrecovered alkyl esters that largely determine the tensile properties, and that BCS can be successfully used to plasticize cast gelatin films as long as the BCS contains 11 parts by weight, or less, of unrecovered alkyl esters per 100 parts glycerol.

**Keywords:** biopolymers, biodegradable polymers, mechanical properties, gelatin, biodiesel glycerol

### 1. Introduction

In biodiesel production, the sale of coproduct glycerol can help to offset the costs of raw materials [1]. However, over the last few years biodiesel production has expanded at rates that have never before been seen. As the amount of available glycerol continues to exceed the market demand, the value of the biodiesel coproduct stream (BCS) has been drastically reduced. Currently, there is a push to find new outlets for BCS in order to help maintain its value. Success in this area would increase the feasibility of fuel production and also improve the economics of biorefinery operations.

Glycerol acts as a plasticizer by reducing the polymer glass temperature, and many applications have been described in the literature. Recent studies continue to illustrate its potential for practical use with both biopolymers and synthetic polymers [2–11]. Stevens *et al.* [12] have recently shown that replacing glycerol with a commercial sample of an unre-

fined BCS did not prevent the formation of viable cast gelatin films, and did not result in the deterioration of tensile properties. Studies of the use of an unrefined BCS as a plasticizer had not previously been reported.

The objective of the present work was to continue to elucidate the potential of using unrefined BCS as a bioplastics plasticizer. The specific aim was to quantify the composition requirements of the BCS necessary in such applications. BCS typically contains, other than glycerol, unreacted fatty acids and unrecovered fatty acid esters. Here we prepared cast gelatin films plasticized with a simulated BCS, i.e., mixtures of glycerol and some of the typical components found in BCS derived from a soy oil or canola oil process (methyl linoleate, methyl oleate, linoleic acid, and oleic acid). The tensile properties were measured as a function of plasticizer composition, and the specific effect of each individual component on tensile properties was analyzed.

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Gelatin was chosen for the present study because it is produced in large amounts for use in a variety of industrial processes, including the manufacture of pharmaceutical products, x-ray and photographic films development, and food processing [13]. It has been used as a component in bone substitute materials [14]. Also, gelatin, unlike some biopolymers, is thermoplastic and can be processed by conventional means, such as extrusion and injection molding [13, 15].

## 2. Materials and methods

### 2.1. Materials

Gelatin (Type A G2500), glycerol, methyl linoleate ( $\geq 99\%$ ), methyl oleate (99%), linoleic acid ( $\geq 99\%$ ), oleic acid ( $\sim 99\%$ ), and ammonium hydroxide (30% aqueous solution) were purchased from Sigma-Aldrich Chemicals.

### 2.2. Film compositions

Previous work [12] had shown that a mid-range composition of gelatin-glycerol cast films, with respect to tensile properties, is approximately 72% gelatin and 28% glycerol. Here, we prepared films with a total weight, excluding water, of 6.0 g, containing 4.32 g gelatin and 1.68 g total plasticizer. The composition of BCS varies with feedstock and biodiesel processing efficiency. As a typical composition we used that previously described [12] in which the organic component, excluding methanol, contained 82% glycerol and 18% other organics. In that sample the other organics were mainly unreacted free fatty acids and unrecovered fatty acid methyl esters, in approximately equal proportions.

We therefore defined a series of simulated BCS mixtures, each containing an organic component of 1.38 g glycerol and 0.30 g of other BCS organic compounds, corresponding to 22 parts by weight per 100 parts glycerol.

Two common sources of biodiesel feedstocks are soy oil and canola oil (low erucic acid rapeseed oil). In both oils, the major fatty acids are linoleic and oleic acids, but the relative amounts (linoleic/oleic) differ, typically 53/23 in soy oil and 21/61 in canola oil [16]. Based on these considerations, we prepared the series of samples with compositions shown in Table 1.

In Table 1, the film compositions are presented in units of grams; the plasticizer (simulated BCS) compositions are described in units of parts by weight of each component per 100 parts glycerol. Sample 1 was a control. In the remaining samples 18% of the glycerol was replaced with BCS components as shown in Table 1. In samples 8 and 9, the fatty acid and methyl ester of both fatty acids were used, in 2:1 and 1:2 proportions, respectively, approximating the proportions in soy oil and canola oil.

Samples were first prepared without the addition of ammonium hydroxide. Those samples, however, showed signs, by visual inspection, of macroscopic film heterogeneity and phase separation; there were visible dispersed droplets, larger than 1 mm in diameter, embedded in the gelatin/glycerol matrix. The films were not characterized further.

The films described herein were prepared with ammonium hydroxide. Previous work [12] had shown that, once dry, there is no free ammonia or ammonia odor.

**Table 1.** Composition [g] of gelatin samples plasticized with BCS components<sup>a</sup>. In parentheses is shown the parts by weight per 100 parts glycerol.

Sample	Glycero	Methyl Linoleate	Methyl Oleate	Linoleic Acid	Oleic Acid
1 <sup>b</sup>	1.68	0	0	0	0
2	1.38	0.30 (21.7)	0	0	0
3	1.38	0	0.30 (21.7)	0	0
4	1.38	0	0	0.30 (21.7)	0
5	1.38	0	0	0	0.30 (21.7)
6	1.38	0.15 (10.9)	0	0.15 (10.9)	0
7	1.38	0	0.15 (10.9)	0	0.15 (10.9)
8	1.38	0.10 (7.2)	0.05 (3.6)	0.10 (7.2)	0.05 (3.6)
9	1.38	0.05 (3.6)	0.10 (7.2)	0.05 (3.6)	0.10 (7.2)
10	1.38	0.075 (5.4)	0.075 (5.4)	0.075 (5.4)	0.075 (5.4)

<sup>a</sup>Each sample contained 4.32 g gelatin. Total weight of gelatin plus plasticizer was 6.0 g.

<sup>b</sup>Sample 1 was prepared in duplicate.



### 2.3 Preparation of films

4.32 g gelatin was added to 2% (v/v) aqueous glycerol solution; the density of glycerol is 1.26 gm/cm<sup>3</sup>. Other components were added according to Table 1. Ammonium hydroxide was added as 6 ml of aqueous NH<sub>4</sub>OH solution (30%). Water was added to bring the total volume to 150 ml. The samples were heated with stirring to 85–95°C in an open beaker. Films were cast, and dried at ambient laboratory temperature and relative humidity.

### 2.4. Morphology

Film samples were optically scanned using a Hewlett Packard ScanJet 5370C and VueScan software.

### 2.5. Tensile properties

Films were stored for four weeks at ambient laboratory conditions prior to tensile testing. Immediately before testing, they were conditioned at a temperature of 23±2°C and relative humidity of 50±5%, according to ASTM Standard Practice D618. Tensile measurements were made on an Instron Model 5543 testing system with a 100 N load cell according to ASTM Test Method D882. Specimen width was 1.27 cm; gage length was 5.08 cm; and test speed was 5.08 cm/min.

### 2.6. Modeling

Tensile properties for the ten samples, with separate values for the duplicates of sample 1, provided eleven data points for the least squares fitting of tensile properties. Tensile properties were modeled

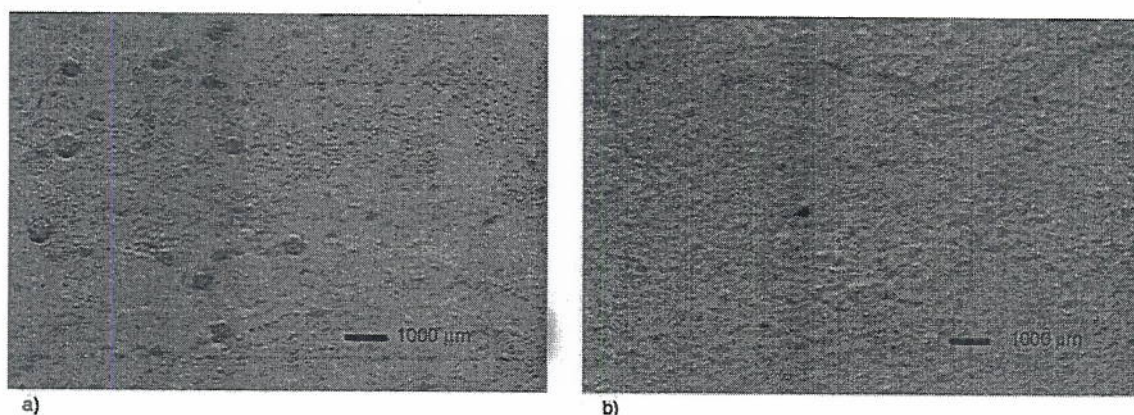
with SAS JMP7 software (SAS Institute, Cary, NC). The Fit Model routine was used with the standard least squares fitting option. Role variables were elongation, modulus, or tensile strength. Effects were the amounts of linoleic acid, methyl linoleate, oleic acid, and methyl oleate. Cross-terms were added if doing so improved the model statistics. Goodness of fit of the model was measured by  $R^2$ , root mean square error, and  $p$  value. Low  $p$  values reflect the statistical significance of the analysis; composition factors with a  $p$  value greater than 0.05 were eliminated.

## 3. Results

### 3.1. Morphology

Sample 1 was clear and showed no signs of phase heterogeneity. Sample 2, containing 22 parts by weight of methyl linoleate per 100 parts glycerol, contained droplets of the methyl ester dispersed within the gelatin/glycerol matrix (Figure 1). The droplets were approximately 1000  $\mu$  in diameter. There were also smaller droplets, approximately 200–300  $\mu$  in diameter. Sample 3, containing the same level of methyl oleate, appeared similar to sample 2.

Samples 4 and 5, containing 22 parts by weight of linoleic acid and oleic acid, respectively, per 100 parts glycerol, appeared macroscopically homogeneous and were indistinguishable from the control. Sample 6 (Figure 1) and samples 7–10, containing only 11 parts by weight of a methyl ester, displayed dispersed droplets distinctly smaller than the 1000  $\mu$  diameter droplets in samples 2 and 3.



**Figure 1.** Optical scans of samples 2 (a) and 6 (b) containing, respectively, 22 and 11 parts by weight of methyl linoleate per 100 parts glycerol



### 3.2. Tensile properties

Results of the tensile measurements, including elongation at break ( $\epsilon$ ), Young's modulus ( $E$ ), and stress at break ( $\sigma$ ), are displayed graphically in Figure 2. Average values and standard deviations are shown;  $N = 5$ . For sample 1, the average of two sample sets of five specimens each is shown. The average sample thickness ranged from 0.15–0.21 mm. Also shown are the previously reported results for a film prepared with a commercial sample of BCS [12].

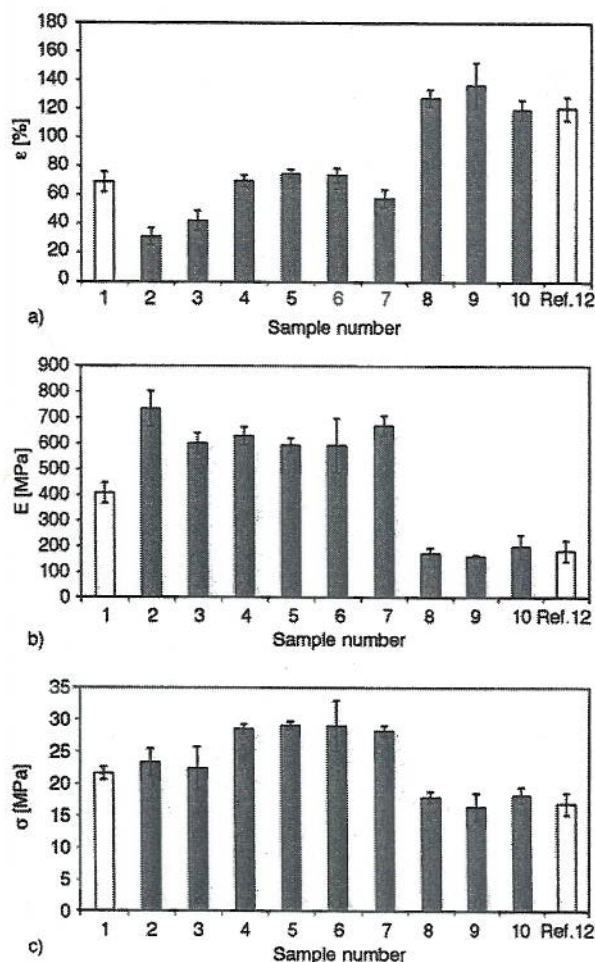
### 3.3. Modeling

A summary of the modeling statistics is shown in Table 2. The fits of all three tensile properties were statistically significant; at least 93% of the variance was accounted for ( $R^2$ ), *rms* (root mean square) values are only slightly larger than or the same as the standard deviations of the individual samples, and all  $p$  values were significantly smaller than 0.05.

## 4. Discussion

### 4.1. Morphology

The films appeared tough and leathery at all compositions; gelatin films plasticized with glycerol and components of BCS are viable films. Methyl esters, when present at a level of 22 parts by weight per 100 parts glycerol (samples 2 and 3), lead to significant film heterogeneities (Figure 1); 1000  $\mu$



**Figure 2.** a) Elongation at break ( $\epsilon$ ), b) Young's modulus ( $E$ ), and c) tensile stress at break ( $\sigma$ ) of cast gelatin films 1–10 described in Table 1. Also shown are the previously reported results for a film prepared with a commercial sample of BCS [12].

**Table 2.** Statistical Results from Modeling Tensile Properties of Gelatin Films<sup>a</sup>

Property/factor	$R^2$	rms error	Scaled estimate	p value
<i>Elongation</i>	0.93	11%		0.0002
Methyl linoleate			108 ± 13	<0.0001
Methyl oleate			110 ± 13	<0.0001
Methyl linoleate × Methyl oleate <sup>b</sup>			306 ± 31	<0.0001
<i>Modulus</i>	0.96	57 MPa		0.0012
Methyl linoleate			−662 ± 72	0.0002
Methyl oleate			−703 ± 72	0.0002
Methyl linoleate × Methyl oleate <sup>b</sup>			−1980 ± 173	<0.0001
Linoleic acid			94 ± 33	0.0342
Oleic acid			103 ± 33	0.0248
<i>Tensile strength</i>	0.94	1.7 MPa		0.0047
Methyl linoleate			−15 ± 2	0.0008
Methyl oleate			−16 ± 2	0.0007
Methyl linoleate × Methyl oleate <sup>b</sup>			−40 ± 5	0.0005
Linoleic acid			3.9 ± 1.0	0.0094
Oleic acid			4.0 ± 1.0	0.0086

<sup>a</sup> $R^2$  is a measure of the variance that is explained by the model; rms is the root mean square error; scaled estimate is a measure of the relative importance of the various factors for a given property. For  $p$  value see text.

<sup>b</sup>A cross term indicates that the effect of one factor depends on the other factor



diameter droplets of methyl ester are dispersed non-uniformly throughout the gelatin/glycerol matrix. Presumably, the heterogeneities are the result of unfavorable interactions between the uncharged fatty acid methyl esters and the disordered gelatin chains, resulting in self-association of the methyl esters.

Free fatty acids, even when present at a level of 22 parts by weight per 100 parts glycerol (samples 4 and 5), are compatible with the gelatin/glycerol matrix; the films are clear and similar in appearance to the control. Presumably, film homogeneity is a result of favorable interactions between the deprotonated fatty acids and the charged side-chains and dipole moments of the disordered gelatin chains.

Films containing only 11 parts of methyl ester per 100 parts glycerol (samples 6–10) appear more homogeneous than films containing 22 parts of methyl ester; the large 1000  $\mu$  diameter droplets observed in samples 2 and 3 (Figure 1) are absent. Ammonium hydroxide improves film homogeneity, regardless of composition. Differential scanning calorimetry results, previously reported [12], showed that ammonium hydroxide prevents the partial renaturation of gelatin during film formation. The present study suggests that it is the maintaining of disordered polymer chains that is responsible for the increase in film homogeneity when ammonium hydroxide is used.

## 4.2. Tensile properties

The low elongations, relative to the control, of films containing 22 parts by weight of methyl ester per 100 parts glycerol (Figure 2a, samples 2 and 3) correlate with those films displaying the greatest phase heterogeneity, and may be a consequence of the heterogeneity. Otherwise, the most notable feature of the tensile properties (Figure 2) is the similarity of samples 2–7, containing only C18:2 molecules (linoleic acid and methyl linoleate) or C18:1 molecules (oleic acid and methyl oleate), but not both. When both types are present, as in samples 8–10, the properties are significantly different; the difference is most notable for the elastic modulus. This result indicates that the interactions of C18:2 molecules with C18:1 molecules are different from the interactions between like molecules, in a way that affects tensile properties. Presumably,

the overall difference in tensile behavior is the net result of polymer-additive interactions, through coefficients of adhesion, on the one hand, and additive-additive interactions, on the other.

It should be pointed out that tensile data for samples 8–10 are consistent with results previously reported for gelatin films plasticized with a commercial BCS which displayed a similar elongation ( $121 \pm 8\%$ ), modulus ( $179 \pm 41$  MPa), and tensile strength ( $16.6 \pm 1.7$  MPa) [12].

The tensile measurements provide quantitative data corroborating the physical description of the films as tough and leathery. It is also worth noting that there is no statistically significant difference between the tensile properties of sample 8, simulating a soy-derived BCS, and sample 9, simulating a canola-derived BCS.

## 4.3. Modeling

The modeling results confirm the important role of unrecovered methyl esters in determining the tensile properties of BCS-plasticized gelatin films. The scaled estimates (Table 2) show that it is the methyl esters that are the main determinants of tensile properties. When both methyl linoleate and methyl oleate are present, methyl esters increase elongation (positive scaled estimates) relative to glycerol and decrease modulus and tensile strength (negative scaled estimates). Significant cross terms between the two types of ester dominate the determination of tensile properties and confirm their interaction; when both are present, their effects are not additive. The fatty acid components play relatively small roles in determining tensile properties.

## 5. Conclusions

Methyl esters, present in BCS as unrecovered products of biodiesel production, play an important role in determining the tensile properties of cast gelatin films plasticized with BCS. Unreacted fatty acids play less of a role. Methyl esters, when present at levels greater than 11 parts by weight per 100 parts glycerol, are poorly incorporated into the gelatin/glycerol matrix, leading to decreased elongations. There are significant interactions between the C18:2 linoleic and C18:1 oleic components. There is no statistically significant difference between the tensile properties of gelatin films plasticized with a



composition simulating a soy-derived BCS and those of gelatin films plasticized with a composition simulating a canola-derived BCS.

In practical terms, the tensile properties of gelatin films could be modulated according to what properties are required. For example, to achieve the same elongation as films plasticized with refined glycerol, a smaller amount of BCS would be required. Also, the possibility exists of using blends of BCS and refined glycerol for additional control of properties.

In the commercial BCS used in the previous study of gelatin films [12], methyl esters were present in only 8 parts by weight per 100 parts of glycerol, which accounts for the homogeneity of the films observed in that study.

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